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Positive magnetoresistance and orbital ordering in $La_{1-x}Sr_xMnO_3$

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We report on detailed transprort measurements of single crystalline $La_{1-x}Sr_xMnO_3$ ($x \leqslant 0.2$). We have found a giant positive magnetoresistance in the compositions range between $0.1 \leqslant x \leqslant 0.125$ and give an explaination in terms of orbital ordering due to the interplay between superexchange interactions and Jahn-Teller distortions.

In the last years an overwhelming interest in the manganite perovskites $La_{1-x}A_xMnO_3$ arose primarily due to the observation of a collosal negative magnetoresistance (CMR) close to $x = 0.3$ [1]. These CMR effects at the ferromagnetic (FM) phase transition were explained within extended double-exchange (DE) models [2–4]. Since then it became clear that this compounds reveal many interesting and puzzling phenomena which can not be accounted for by double exchange alone. It was Millis et al. [5] who first related dynamic Jahn-Teller (JT) distortions to the CMR effect. In a recent paper [6] we have presented a detailed phase diagram of $La_{1-x}Sr_xMnO_3$ at low Sr concentrations. In the concentration regime $0.1 \leqslant x \leqslant 0.15$ we detected a ferromagnetic (FM) and insulating (I) ground state which is followed by a canted antiferromagnetic (CA) or mixed phase at elevated temperatures [6]. This insulating FM-phase results from superexchange (SE) interactions in a charge-ordered (CO) phase which probably also reveals orbital order.

In this paper we will present detailed transport measurements on $La_{1-x}Sr_xMnO_3$ single crystals. It will be shown that the double degeneracy of the e_g orbitals and their ordering in real space must be considered in order to understand the ferromagnetic and insulating ground state in this doping regime. Recently theoretical models considered the orbital degrees of freedom, but have mainly focused on the properties of the $LaMnO_3$ and $La_{0.5}Sr_{0.5}MnO_3$ compounds [7]. Although Ahn and Millis [8] discussed the interplay of orbital and charge ordering for $La_{0.875}Sr_{0.125}MnO_3$ they did not considered the effect of this types of ordering on the mangetic properties. Using a mean field approximation Maezono *et al.* [9] have obtained an overall phase diagram of doped manganites based on the interplay of SE- and DE-interactions.

Here we provide strong experimental evidence that the competition between JT-, SE- and DE-interactions is responsible for the rich variety of magnetic and structural phase transitions in the low doping phase diagram ($x \leqslant 0.2$). At the phase boundary of the insulating FM ground state, a strong (collossal) positive MR appears. We will show that the close coupling of structural and magnetic phase transitions and especially the magnetic field induced structural transitions can only be explained assuming orbital order in the O´´-phase.

Single crystals of $La_{1-x}Sr_xMnO_3$, with concentrations $0.1 \leqslant x \leqslant 0.2$ were grown by a floating zone method with radiation heating in air atmosphere. X-ray diffraction of crushed single crystals revealed high-quality single-phase materials. X-ray topography indicated twinning of the crystals. Transport measurements in the temperature range 1.5-300 K were performed with the standard four-probe method in fields up to 14 T.

The relevant part of the phase diagram around $x = 0.125$ is reproduced in Fig. 1. Close to this concentration a rather unusual sequence of phase transitions has been detected. At room temperature $La_{0.875}Sr_{0.125}MnO_3$ is orthorhombic. A long range JT distortion (and hence orbital order) appears at $T_{OO'}$=265 K, both orthorhombic phases beeing insulating [10]. At T_{CA}=180 K a CA structure is established where the resistivity is reduced almost by a factor of 10. It is this regime which has been treated as a FM and metallic phase during the last years. This however was not based on experimental results but only due to the fact that $d\rho/dT > 0$ in a limited temperature regime and that a FM regime which is followed by a canted spin structure at lower temperatures nicely fits into de Gennes phase diagram [3]. We have shown that this phase reveals a canted structure [6]. Of course, we also can not exclude a mixed phase in this regime, but it is definitely not metallic. The decrease in the resistivity probably indicates an increase of the charge transfer matrix elements due to the increasing importance of the DE mechanism combined with the freezing out of spin-disorder. Finally at $T_{O'O''}$=150 K and T_C=140 K a structural phase transition is immediately followed by the onset of FM order [6]. The O´´-phase reveals charge order in an almost pseudocubic lattice and the ground state is a FM insulator.

The field dependence of the magnetoresistance ($\Delta\rho/\rho(0)$=ρ(H)-ρ(0)/ρ(0)) for $x = 0.1$ and $x = 0.125$

is shown in Fig. 2 for various temperatures. For temperatures $T>T_{O'O''}$ we find negative MR effects. However we would like to point out that here the negative MR appears at the transition from a paramagnetic (PM) insulator into a CA or mixed phase. Small negative MR effects again appear for $T<T_C$=105 K. However, between $T_{O'O''}$ and T_C large or even colossal positive MR effects appear, due to the fact that the FM ground state is indeed more insulating than the CA phase. A closer inspection of Fig. 2 reveals that two subsequent jumps appear as a function of increasing field. Both jumps induce higher resistivity states and correspond to those ones observed in the magnetization curves (see Fig. 3 in [6]). The first jump is due to a field induced structural phase transition from the JT-distorted O´- to the pseudocubic O´´- orthorhombic phase and obviously is accompanied by a real space charge ordering of the Mn^{3+} and Mn^{4+} ions [11]. At the subsequent second jump the sample undergoes a transition into a FM state with the magnetoresistance showing a saturated behavior at higher fields. For $x = 0.125$ these jumps are not clearly separated, a fact that has also been observed in the magnetization curves. In contradiction to the $x = 0.1$ compound, the magnetoresistance of the $x = 0.125$ sample decreases with increasing field below the field induced transition to the charge ordered FM state. Finally for the $x = 0.15$ sample (not shown) only negative CMR effects have been observed in agreement with previous published results [12]. It is remarkable that in the temperature range between T_{CA} and T_C the magnetoresistance at a given field changes sign and becomes positive.

To show these large positive MR effects, the temperature dependence of the magnetoresistance for various fields and doping levels is plotted in Fig 3. For $x = 0.1$ two pronounced peaks yielding an increase in resistivity up to +400% when the magnetic field is raised to 5 T are clearly visible. These peaks corresponds to the transitions into the O´´- and FM-state respectively. Around T_{CA} the typical negative MR effect can be seen. The same features are also present for $x = 0.125$, though the two positive enhachments at $T_{O'O''}$ and T_C obviously merge resulting into a single peak. The positive MR is maximal for $x = 0.1$, becomes significant smaller for $x = 0.125$ and finally dissappears for $x \geqslant 0.15$. Summarizing the magnetoresistance measurements indicate a large positive MR at the transitions O´/CA→O´´/CA and O´´/CA→O´´/FM, while negative MR effects appear close to the O´/PM→O´/CA and O/PM→O/FM phase boundaries (see Fig. 1). The negative MR obviously result from the onset of spin order below T_{CA} (i.e. T_C for $x > 0.15$) and can be explained within a double-exchange picture as proposed by [2]. The electronic properties in the O´´-phase are more complicated and can not be explained taking only double-exchange interactions in account.

Finally in Fig. 4 we show a H-T-phase diagram for $La_{0.9}Sr_{0.1}MnO_3$. We choose this concentration as for this sample the sequence of two strongly coupled phase transitions (O´→O´´, CA→FM) can be easily documented (see e.g. Figs. 2 and 3). The insulating region of positive MR is enbedded in insulating phases which reveal negative MR effects. Both transition temperatures ($T_{O'O''}$, T_C) are shifted to higher temperatures as the external field is increased. At the two closely related phase boundaries $T_{O'O''}$ and T_C three degrees of freedom, namely the charges (Mn^{3+}/Mn^{4+}), the spins and the orbitals undergo an ordering process. The structural phase transition $T_{O'O''}$ indicates charge ordering [11] and most probably also orbital ordering.

We start our discussion summarizing the most important experimental results presented here. It is obvious that the transition from the canted-AFM and JT-distorted O´-phase to the pseudocubic charge-ordered O´´-phase is intimately coupled to a transition into an insulating FM state. The positive CMR effect observed in the vicinity of the commensurate doping value $x = 0.125$ counts for a very different picture as it can be given by the interplay of JT-distortion and DE-interactions alone.

It is well know that the double degeneracy of the e_g levels of $3d$ ions in an octahedral enviroment is lifted by an JT-distortion of the lattice [13], accompanied by an ordering of the orbitals in real space. The possibility of orbital ordering in transition-metal ions due to exchange interactions different than that resulting from JT-distortions was first pointed out by Roth [14] and has been extensively studied by Kugel and Khomskii [15]. It has been shown that two transitions take place, one into an orbitally ordered state and a second into a spin-ordered state, both driven by SE-mechanisms. This SE differs from the ordinary one due to the fact that each electron has four degrees of freedom, two orbital states (d_{z^2}, $d_{x^2-y^2}$) and two spin states (spin-up, spin-down). The presence of intra-atomic exchange in case of orbital degeneracy produce ferromagnetism below the orbital-ordering phase transition [16]. It is important to notice that above the orbital-ordering transition temperature the effective spin-spin interaction is AFM, which is modified by the appearance of the orbital ordered state and finally goes over into a FM coupling. A modern view of this problem has been recently considered by Held and Vollhardt [17].

For undoped $LaMnO_3$ the magnetic properties can be well explained taking only the predominant JT-distortion of the MnO_6 octaherda into account. The double degeneracy of the e_g orbitals is lifted by a long range cooperative Jahn-Teller distortion resulting in an ordering of the d_{z^2} orbitals as has been argued by Solovey *et al.* [18] and has recently been confirmed experimentaly by Murakami *et al.* [19]. As a result of this JT driven orbital ordering the A-type AFM state is established below T_N.

Upon doping with holes the long-range JT-distortion become suppressed and concomitantly double-exchange

interactions have to be taken into acount. At room temperature the lattice is distorted as in $LaMnO_3$ (O´-phase) due to the JT effect removing the double degeneracy of the e_g levels. Since mobile holes are present, the double exchange mechanism plays a fundamental role. The magnetic structure observed in undoped $LaMnO_3$ is modified by the appearance of three-dimensional ferromagnetic DE-interactions, competing with the JT driven A-type AFM yielding a canted AFM state (or mixed phase). Thus canted antiferromagnetism is established below T_{CA}=150 K, accompanied by a drop in the resistivity, since a gain in kinetic energy of the carriers due to DE-interactions can be achieved. Further lowering of the temperature favours SE-interactions between Mn^{3+} ions in a manner discussed above, yielding the ordering of orbitals and subsequently the evolution of ferromagnetism. At $T_{O´O´´}$ the SE-interactions become dominant, suppress the JT-distortion and enforces the structural transition into the pseudocubic O´´-phase, followed by the onset of ferromagnetism at T_C. At the same time an insulating behavior appears due to charge and orbital ordering, which decreases the hole mobility and explains the positive jumps in the MR curves. The transition to the orbital ordered FM state, is stabilized by the application of an external magnetic field as can be seen in Fig. 1 and Fig. 2. We remind that by application of an external magnetic field jumps in the magnetization curves has been observed, leading the sample to higher magnetization states [6]. This field induced transitions can not be ascribed to magnetocrystalline anisotropy since no dependence was found for different orientations of the crystal axes in respect to the applied external field. The possibility of magnetic field induced transitions due to the interplay of the JT-effect and SE-interactions has been first pointed out by Kugel and Khomskii [20]. It was shown that when orbital ordering is enforced by the SE mechanism such transitions are possible. On the other hand if orbital ordering is established due to electron-lattice interactions (JT-effects) as it is believed to be in $LaMnO_3$, then such transitions may not appear.

At the moment only predictions about how the orbitals are ordered in the low temperature state can be made, but an alternation of occupied d_{z^2} and $d_{x^2-y^2}$ orbitals on neighbouring Mn^{3+}-sites appear most probably to us (Fig. 5). This would cause a displacement of the O^{2-} ions due to secondary electrostatic interactions [15], yielding alterning long and short Mn-O bonds. Together with the real space ordering of the Mn^{3+}/Mn^{4+} ions this would result in additional superstructure reflections in the diffraction patterns. Finally for doping levels higher than $x \geqslant 0.175$ the double exchange mechanism becomes dominant and a metallic ferromagnetic state is established. The orbital liquid picture recently proposed by Ishihara *et al.* [21] may be appropriate to describe the physics in the metallic phase.

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FIGURE CAPTIONS:

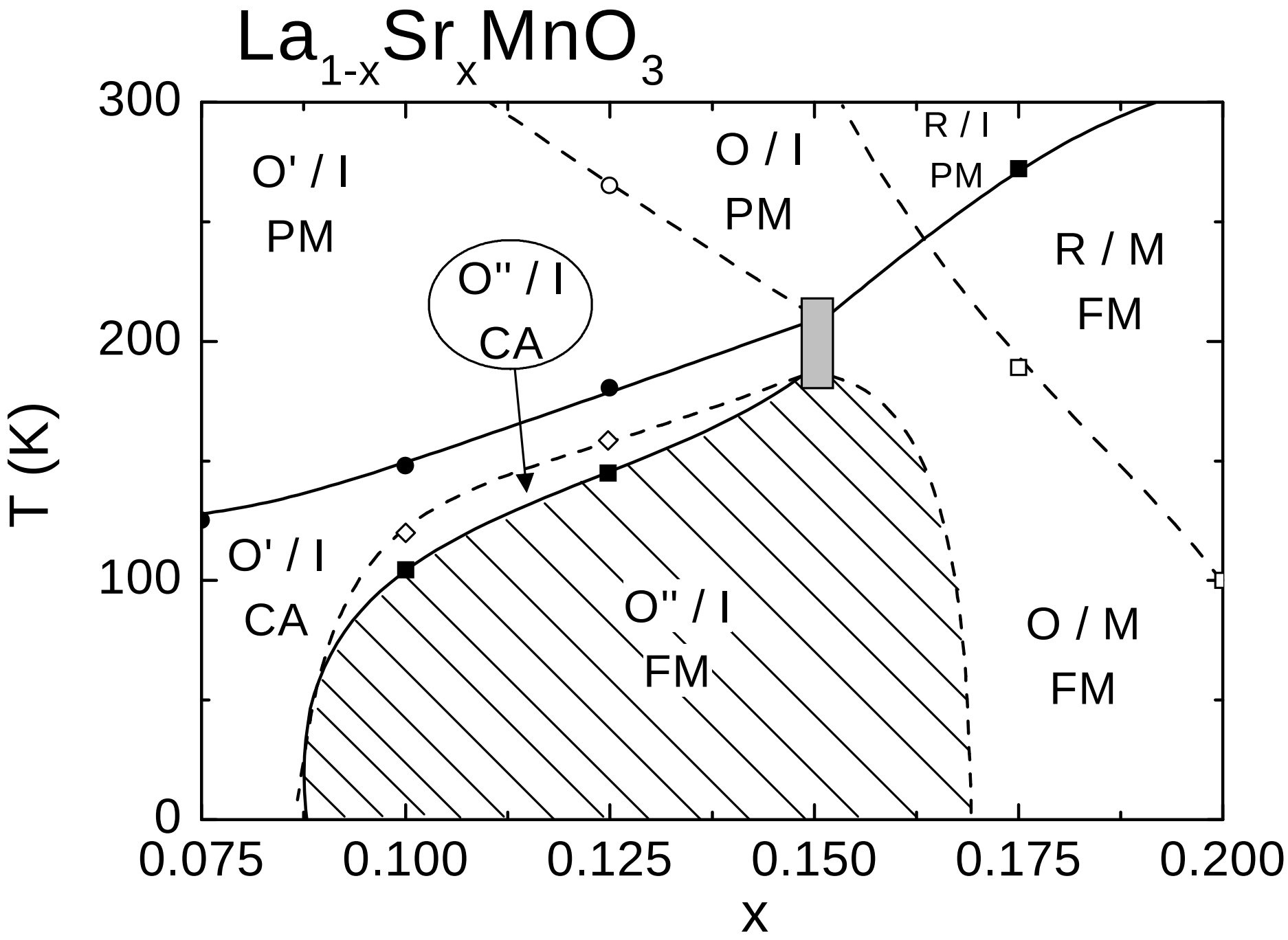
Fig. 1: Phase diagram of $La_{1-x}Sr_xMnO_3$ at low doping concentrations. The shaded area represents an orbitally and charge ordered insulating ferromagnet.

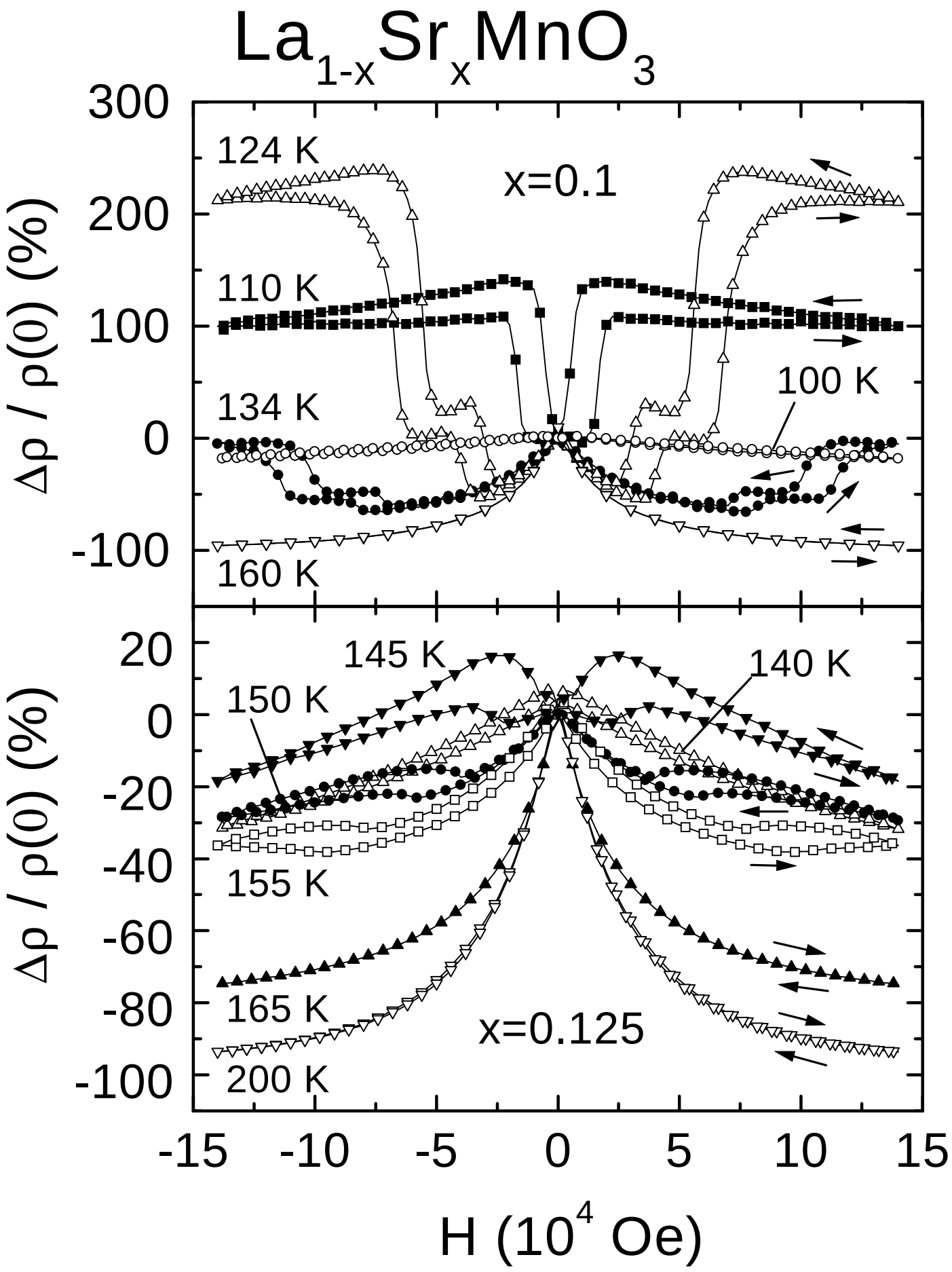
Fig. 2: Isothermal magnetoresistance curves for the $x = 0.1$ and $x = 0.125$ samples.

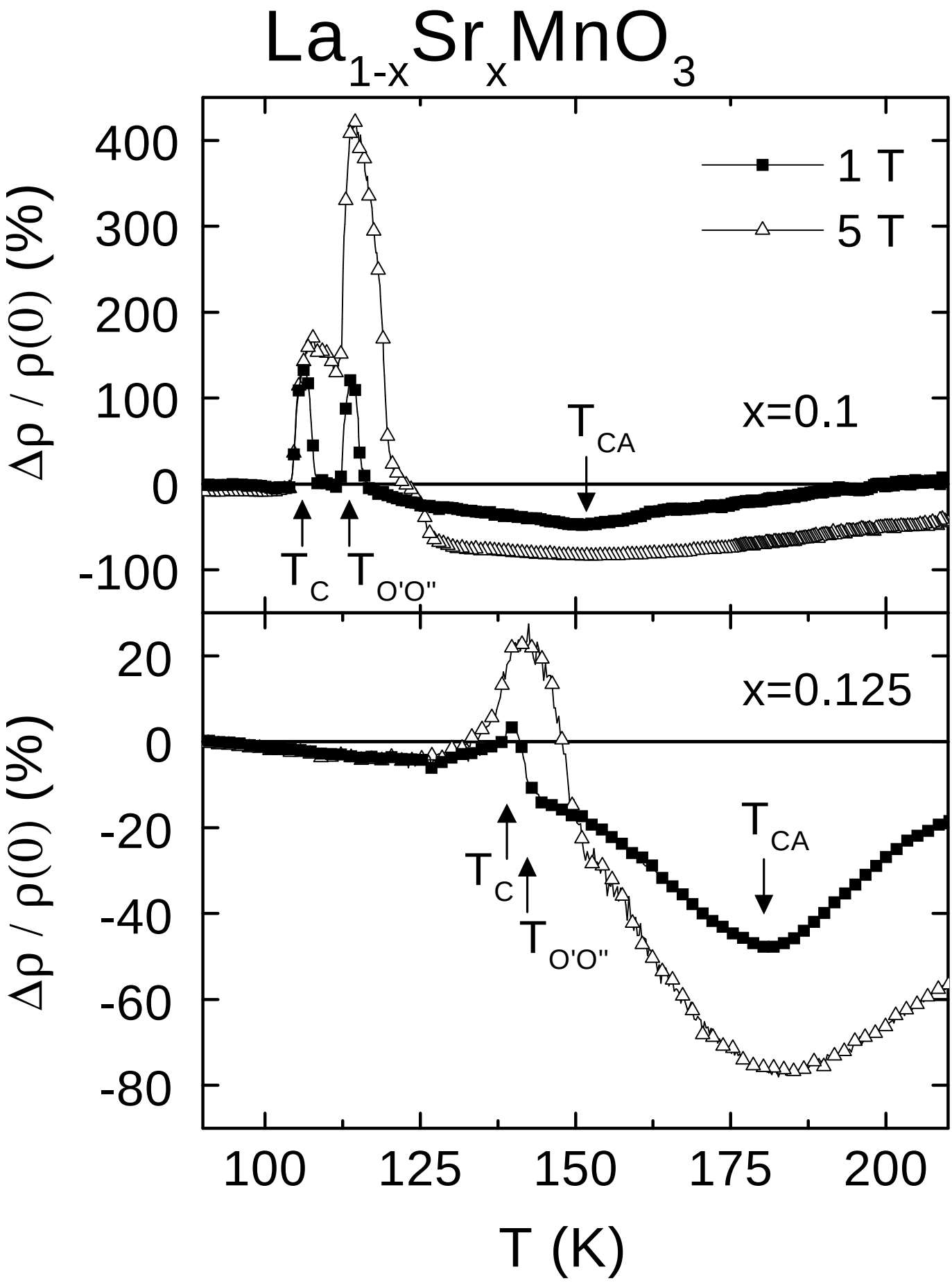
Fig. 3: Temperature dependence of the MR for $x = 0.1$ and $x = 0.125$ at various applied magnetic fields.

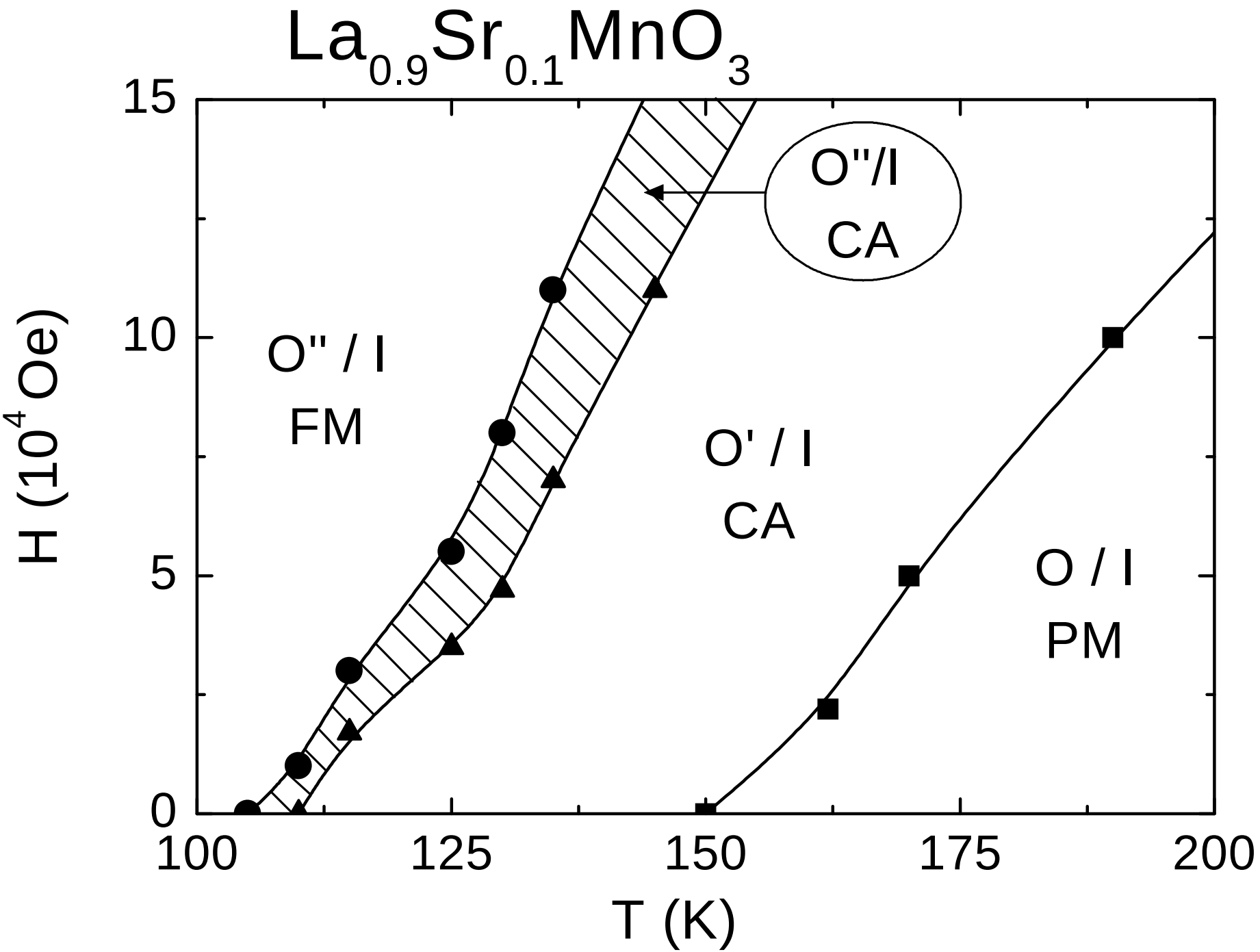
Fig. 4: H-T-phase diagram for $x = 0.1$. The shaded area corresponds to the region of positive MR. A strong negative MR appears close to the OO´-phase boundary.

Fig. 5: Orbital ordering in $La_{0.875}Sr_{0.125}MnO_3$ which is in accord with the charge order proposed by Yamada *et al.* [11].


La1-xSrxMnO3
300
200
100
0
T (K)
0.075
0.100
0.125
0.150
0.175
0.200
x
O' / I
PM
O / I
PM
R / I
PM
R / M
FM
O'' / I
CA
O' / I
CA
O'' / I
FM
O / M
FM


La1-xSrxMnO3
300
200
100
0
-100
Δρ / ρ(0) (%)
124 K
x=0.1
110 K
100 K
134 K
160 K
20
0
-20
-40
-60
-80
-100
145 K
140 K
150 K
155 K
165 K
x=0.125
200 K
-15
-10
-5
0
5
10
15
H (10^4 Oe)


La1-xSrxMnO3
400
300
200
100
0
-100
Δρ / ρ(0) (%)
1 T
5 T
x=0.1
TCA
TC
TO'O''
20
0
-20
-40
-60
-80
Δρ / ρ(0) (%)
x=0.125
TCA
TC
TO'O''
100
125
150
175
200
T (K)


La0.9Sr0.1MnO3
15
10
5
0
H (10^4 Oe)
100
125
150
175
200
T (K)
O''/I
CA
O'' / I
FM
O' / I
CA
O / I
PM

$La_{0.875}Sr_{0.125}MnO_3$

Mn^{3+}

d_{z^2} orbital

Mn^{3+}

$d_{x^2-y^2}$ orbital

Mn^{4+}